

# **Sediment Mixing in Coastal Regions: The Impact of Animal Digestion on Radionuclide Tracers**

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## **LONG-TERM GOALS**

We focus on measurement of, and controls on, bioturbation in marine sediments. We seek to further our understanding of the solubilization of metallic elements during passage of marine sediments through the digestive systems of deposit feeders. Of particular interest are the implications of this solubilization for the dissolution of metallic contaminants in sediments and the metallic radionuclides used in measuring sediment bioturbation.

## **OBJECTIVES**

We will test for the chemical mechanisms by which various metals are solubilized by the ligands present in digestive fluids. We hope to isolate specific ligand groups involved in binding the metals. We will also test if metallic radionuclides used in bioturbation, such as  $^{234}\text{Th}$  and  $^{210}\text{Pb}$ , are significantly solubilized by digestive fluids. If so, we will assess which matrices holding these radionuclides are particularly vulnerable to the dissolution process. We will determine the frequency of gut passage in the field and explore the use of biomarkers, such as chlorophyll and carotenoid pigments, as indicators of gut-passage frequency. Implications for published and developing models of bioturbation will be assessed based on these results.

## **APPROACH**

Initially, our general approaches were to (1) to conduct incubation experiments with gut fluids of deposit feeders to assess the amount of metallic radionuclides solubilized from the sediments, (2) to determine both intrinsic (organismal) and extrinsic (sedimentary) factors contributing to the solubilization, and (3) to corroborate the incubation experiments with *in vivo* solubilization and bioaccumulation measurements. A fourth approach, developed during this project, was to determine the products of phytoplankton-pigment degradation during deposit-feeder gut passage and seek these compounds in field samples as markers for gut passage. This work was carried out with the participation of two post-doctoral fellows – Z. Chen and D. Shull, as well as collaboration with D. Weston (U.C./Berkeley).

## **WORK COMPLETED**

We examined which ligands in gut fluid were important in the solubilization of metallic elements, using a series of blocking agents that prevent different functional groups from binding to metals. Focus

was on sulfhydryl, imidazole, and carboxylate groups. This work was carried out for Pb, Cd, Zn, Fe, Mn and Hg.

Via a series of laboratory experiments we examined the dissolution of radionuclides in deposit-feeder digestive fluids. These experiments addressed the roles of solids concentrations, kinetics and phase transfer between algal detritus and bulk sediment. We also performed preliminary experiments examining degradation of phytoplankton pigments in deposit-feeder digestive fluids.

We sampled two sites in the Damariscotta Estuary, coastal Maine, with a box corer. These samples are were analyzed over the past year for phytoplankton pigments, radionuclides, benthic infauna, X-ray radiography, and a variety of indicators of food quality and sediment bulk properties.

## RESULTS

Our work with copper showed that protein binding can affect enzyme function in gut fluids. This inhibition decreases with increasing background concentration of proteinaceous materials in the gut fluid among species. Extension of the ligand blocker approach to metals other than copper showed more complex patterns of gut fluid binding than was found for copper. Our previous results indicating multiple linkages for Pb was recently corroborated by results for Cd, Hg and Zn. Carboxylate binding was present, though not dominant, for all three metals. Cd showed more significant binding by both imidazole groups (presumably histidine residues) and sulfhydryl groups (perhaps cysteine residues). Zn also showed minor binding by both imidazole and sulfhydryl groups. These binding patterns are consistent with a dominant role for dissolved proteins, presumably a combination of digestive enzymes and hydrolyzed food proteins, in binding metals in gut fluids. Results for Fe and Mn were less clear and likely related to redox reactions.

We found significant gut fluid dissolution of a suite of radioisotopes, including  $^{234}\text{Th}$ ,  $^{210}\text{Pb}$ ,  $^7\text{Be}$ , and  $^{137}\text{Cs}$  from algal detritus or sediment particles. Kinetics experiments showed that most dissolution reactions occur within minutes, although  $^{234}\text{Th}$  can require hours to reach steady state. We found appreciable gut fluid dissolution of  $^{234}\text{Th}$ ,  $^{210}\text{Pb}$ , and  $^7\text{Be}$  from algal detritus labeled with these isotopes.  $^{137}\text{Cs}$  was also desorbed from clays at low concentrations in gut fluid. Further experiments examined the partitioning of radionuclides among algal, mineral, and digestive-fluid phases. Upon addition of unlabeled sediment particles in concentrations ranging up to those found in *A. marina* midguts, little net dissolution occurred, indicating that dissolved radionuclides were resorbed by solid phase ligands associated with minerals. Algal detritus can resorb these radionuclides with higher affinity than sediment, perhaps indicating the presence of high-affinity bacterial ligands that have previously been described in water column studies. These results provide a mechanism for the observation that radionuclides with short half-lives are mixed more rapidly than those with longer half-lives. Cumulative gut passages will redistribute a greater fraction of longer-lived tracers onto mineral phases, which are selected less frequently by deposit feeders than organic particles enriched in both nutritional content and water column-derived radioisotopes.

Our laboratory experiments with phytoplankton pigments have explored the kinetics and extent to which chlorophylls and carotenoids are degraded during gut passage, and show that significant but not complete degradation can be expected within normal gut residence times. Certain chlorophylls and carotenoids were found to be rapidly degraded in deposit feeder guts, with half-lives of about 15 min in both a polychaete and a holothuroid. This decay could be only partially reduced by inactivating the animals' digestive enzymes by microwave treatment.

Downcore profiles indicated active mixing of sediments – to ca. 10 cm at one site and perhaps to >20cm at another site although this latter site may have instead undergone rapid deposition. Bioavailable protein levels (as enzymatically hydrolyzable amino acids, or EHAA) were higher than 0.4 mg/g throughout the mixed zones of the cores. Sub-surface peaks in EHAA concentrations were found in each core, corresponding with peaks in  $^{210}\text{Pb}$  activities and/or plant pigment concentrations (especially fucoxanthin). These peaks imply rapid subduction of food-rich, likely diatomaceous, material. These results will be joined with innovative modelling approaches to determine pigment decay kinetics and gut passage frequency of various particle types assuming nonlocal transport events.

## **IMPACT/APPLICATIONS**

The results from radioisotope experiments indicate that deposit feeders can dissolve algal-bound, particle-reactive radionuclides used in measurement of bioturbation rates. The matrix that binds these nuclides may shift from algae, or other labile food substrates, to mineral surfaces due to deposit-feeder gut passage. These findings indicate that chemical changes due to gut passage may be as important in bioturbation modeling as spatial displacement of sediment during gut passage, because the nuclides shift from a phase likely selected by deposit feeders to one not as selected. As bioturbation models begin to account for particle selection this shift will need to be taken into consideration. Our studies of phytoplankton pigment degradation in deposit feeder digestive fluids indicate that these may be useful indicators of deposit-feeder gut passage in the field and could be measured in combination with radionuclides to determine both sediment mixing and gut passage frequency in the field. The ligands responsible for metal dissolution are a mixture of different types typical of those found in proteins, so that mimicry of gut fluid dissolution must use similarly complex ligand assemblages.

## **TRANSITIONS**

Our results from the ligand-blocking experiments are being used to develop an artificial gut fluid to measure bioavailable contaminants in harbor dredge spoils, in a project funded by the U.S. Army Corps of Engineers. This artificial gut fluid will consist of materials similar in structure and function to those found in natural gut fluid, providing a biomimetic capability to environmental risk assessment in an easier and less expensive methodology that will allow for more accurate environmental decision-making.

## **RELATED PROJECTS**

Our ligand identification and ongoing frequency of gut passage work enhance the basis for our Corps of Engineers project. Our results from both radionuclide dissolution during gut passage experiments and field work on estuarine sites will be transitioned to our current Depscor project on nutritional control of bioturbation. The results from metal surveys in deposit-feeder gut fluids has benefited an ongoing study of binding of organic contaminants, as metals may provide the instigation for oxidative coupling reactions that immobilize PAH metabolites.

## **PUBLICATIONS**

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